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DIFFUSION OF URANIUM IN MOLYBDENUM, NIOBIUM, ZIRCONIUM, AND TITANIUM

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Investigations on diffusion of uranium in molybdenum, niobium, zirconium, and titanium by alpha radiation of U^{235}-enriched uranium at 915 - 2000°C are reported, with data on the temperature dependence of the diffusion coefficients. The obtained low activation energy of diffusion in zirconium and titanium is attributed to the polymorphous $\alpha \rightleftarrows \beta$ transformation, resulting in atomic defects such as excess vacancies and thus causing a decrease in activation energy and an increase in diffuse mobility.

The diffusion of uranium in molybdenum, niobium, zirconium, and titanium was investigated. The diffusion coefficients were determined by measuring the integral activity of the residue of the specimen using α-radiation of uranium enriched to 90% by the isotope U^{235}, at temperatures of 1500 - 2000°C (molybdenum, niobium) and 915 - 1200°C (zirconium, titanium).

The temperature dependence of the diffusion coefficients is represented */522 by the equations:

$$D^{U}_{Mo} = 7{,}60 \cdot 10^{3} \exp(-76\,400/RT)\ cm^2/sec;$$
$$D^{U}_{Nb} = 8{,}90 \cdot 10^{-3} \exp(-76\,800/RT)\ cm^2/sec;$$
$$D^{U}_{Zr} = 7{,}77 \cdot 10^{-5} \exp(-25\,800/RT)\ cm^2/sec;$$
$$D^{U}_{Ti} = 4{,}90 \cdot 10^{-4} \exp(-29\,300/RT)\ cm^2/sec.$$

The substantial differences in the diffusive mobility and in the values of

* Numbers in the margin indicate pagination in the original foreign text.

the activation energy of molybdenum and niobium on one hand and zirconium and titanium on the other are probably caused by crystal lattice defects such as excess vacancies, occurring in zirconium and titanium during polymorphous transformation.

Previous investigations of diffusion in systems with uranium mainly included studies on self-diffusion in pure uranium and its alloys, as well as chemical and reactive diffusion (Bibl.1 - 5). The results of these investigations are of definite interest in the development of uranium alloys and in studying the character and kinetics of the interaction of uranium and other metals. Comparatively few data have been published on the diffusion of uranium in pure metals at low concentration gradients. The results of such investigations can be used in estimating the penetration of uranium under conditions where small uranium concentration gradients occur on the surface of contacting materials.

In this study, the diffusion of uranium in molybdenum, niobium, zirconium, and titanium was investigated. The diffusion coefficients were determined by the integral residue method (Bibl.6) with the use of α-radiation of uranium enriched to 90% with the isotope U^{235}. For the investigation, we used molybdenum (99.98% Mo; 0.001% Ti; 0.008% Fe; 0.006% Si; 0.001% W), niobium (99.55% Nb; 0.03% Cu; 0.07% Fe; 0.01% Mo; 0.11% Si), zirconium (99.61% Zr; 0.01% Cu; 0.04% Fe; 0.01% Ni), and titanium (99.62% Ti; 0.07% Fe; 0.01 Mo; 0.01% Si). Specimens of these metals were pre-annealed at 1500°C (molybdenum, niobium) and 1000°C (zirconium and titanium). The uranium was applied to the specimens as a thin layer of about 0.1 μ thickness by spraying in vacuo (vacuum $\sim 10^{-5}$ mm Hg). Homogenizing of the zirconium and titanium specimens at 915 - 1200°C was done in resistance furnaces with nichrome and carborundum heating elements. During the

treatment, the specimens were kept in a vacuumtight quartz ampoule which had been pre-exhausted to a residual pressure of 10^{-4} mm Hg. To prevent possible oxidation, the specimens were packed with titanium or zirconium shavings. The temperature was measured by a platinum platinum-rhodium thermocouple with an accuracy to within $\pm 5^{\circ}C$.

Homogenizing of the molybdenum and niobium specimens at 1500 - 2000°C was done in a high-temperature vacuum furnace with a tungsten heating element at a residual pressure of $(3 - 5) \times 10^{-5}$ mm Hg. In this case, the temperature was measured by a tungsten-rhenium thermocouple calibrated with respect to the melting points of the pure metals. The accuracy of the temperature measurement was $\pm 10^{\circ}C$. The homogenizing time varied from 1 to 20 hrs. The depth of penetration of uranium amounted to 50 - 200 μ. The thickness of the removable layers was determined by the difference in values of the thickness of the specimens before and after removing the layer with an accuracy to within 2 - 3 μ. The activity was measured on a B-2 radiometer with a scintillation attachment. The measuring time was selected such that the relative error did not exceed ± 1%. Under these conditions the relative error of measuring the diffusion coefficients was ~ 12% and that of determining the activation energy ~ 5%.

The diffusion coefficient was determined by the integral residue method (P.L.Gruzin's method). For α-radiation the standard working formula has the form

$$\ln I_n = A - \frac{x_n^2}{4Dt},$$

where I_n is the integral activity of the residual specimen after removing a layer of a thickness x_n; A is a constant; D is the diffusion coefficient; t is the homogenizing time.

Figures 1 and 2 show the curves for the temperature dependence of the dif-

fusion coefficient. The values of the activation energy ΔH and of the frequency factor D_0 calculated from these curves are given below:

Metal	Activation Energy, cal/gm • atom	Frequency Factor, cm^2/sec
Molybdenum ..	76,400	7.60×10^{-3}
Niobium	76,800	8.90×10^{-2}
Zirconium ...	25,800	7.77×10^{-5}
Titanium	29,300	4.90×10^{-4}

It is apparent from these data that the diffusion of uranium in molybdenum and niobium is characterized by comparatively high values of the activation /523 energy. This result corresponds to the high melting point and activation energy of self-diffusion in molybdenum (T_{mp} = 2620°C; ΔH = 92,400 - 115,000 cal/gm • • atom) (Bibl.7, 8) and in niobium (T_{mp} = 2470°C; ΔH = 84,000 - 105,000 cal/gm • • atom) (Bibl.9, 10). However, the activation energy of diffusion of uranium in molybdenum and niobium is below the corresponding values for self-diffusion in these metals. This indicates that the uranium atoms are less strongly bound in the lattice of molybdenum and niobium than the atoms of the base metal. This corresponds to the fact that alloying of molybdenum and niobium with uranium leads to a decrease in melting point.

The activation energy of diffusion of uranium in zirconium and titanium is appreciably lower than the above-indicated values for molybdenum and niobium. Zirconium and titanium, despite their comparatively high melting point, have abnormally low values of the activation energy of self-diffusion and diffusion of metal admixtures. Thus, for the temperature range of 900 - 1200°C, the experimental values of the activation energy of self-diffusion in β-zirconium (24,000 to 38,000 cal/gm • atom) (Bibl.11, 12) and β-titanium (31,200 cal/gm • atom) (Bibl.13) is one-half to one-third that of the calculated value (70,000 to

80,000 cal/gm • atom).

It follows from this that the low values of the activation energy of diffusion of uranium in zirconium and titanium obtained in our investigation cor-

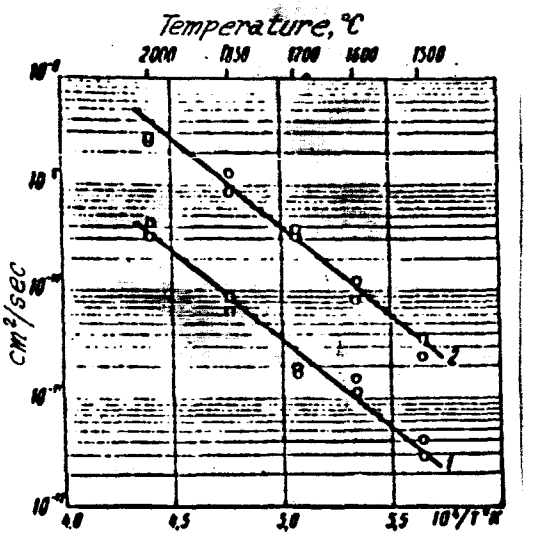

Fig.1 Temperature Dependence of the Diffusion Coefficient of Uranium in Molybdenum (1) and in Niobium (2)

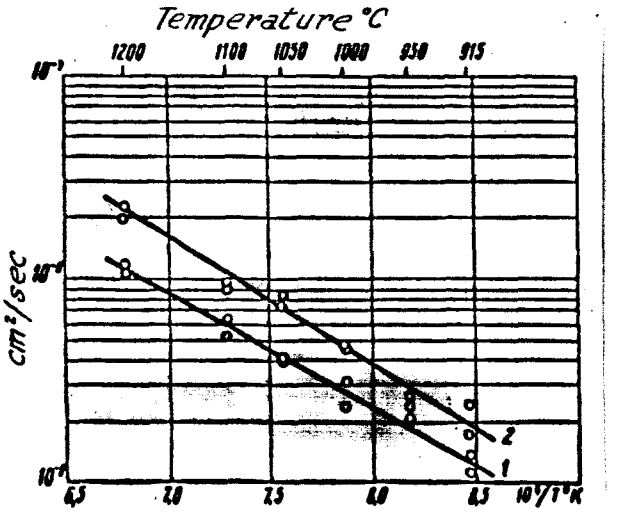

Fig.2 Temperature Dependence of the Diffusion Coefficient of Uranium in Zirconium (1) and Titanium (2)

respond to the data on self-diffusion in these metals. In our opinion, the observed anomalies are due to the effect of the polymorphous $\alpha \rightleftarrows \beta$-transformation

in zirconium and titanium, causing the development of atomic defects, for example, excess vacancies. As a consequence, the activation energy decreases and the diffusive mobility increases.

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